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## EUROPEAN PATENT APPLICATION

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54 Method of separating zirconium isotopes.

57 Method of altering the zirconium 91 isotopic content of zirconium by raising a zirconium chelate ligand from a ground state to an activated state in the presence of a scavenger which reacts with the activated state but not with the ground state, and permitting from 25 to 75% of the zirconium chelate to react with the scavenger. The reaction may be performed in a solution of the zirconium chelate ligand using water as a solvent. Activation of the zirconium chelate may be accomplished by using light and having a wavelength of from 220 to 350 nm or by heating to from 80 to 100 °C.

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## METHOD OF SEPARATING ZIRCONIUM ISOTOPES

This invention relates to a method of separating zirconium isotopes.

Due to its low absorption of neutrons, zirconium is very useful as a container for nuclear fuel rods.

5 There are five common isotopes of zirconium, atomic weights 90, 91, 92, 94, and 96, the abundance of which in natural zirconium is 52, 11, 17, 17, and 3%, respectively. The 90 isotope has a very low neutron absorption cross-section, and is therefore an ideal fuel rod cladding, but the 91 isotope has an absorption cross-section about 10 times that of the 90 isotope. Thus, the efficiency of a nuclear reactor can be greatly increased if the 91 isotope is removed from the zirconium used to clad the nuclear fuel. This can be accomplished by a laser isotope process in 15 which a zirconium compound such as zirconium tetrachloride or zirconium tetrapropoxide is exposed to a laser tuned to a wavelength which is absorbed by only the 90 or the 91 isotope. The light excites only the isotope which absorbs it and only the excited isotope reacts with a scavenger to 20 form an easily separated reaction product. While the laser isotope process can produce a pure zirconium 90 isotope, it is a very expensive process.

An article by Bernhard Kraeutler and Nicholas J. Turro in Chemical Physics Letters, Volume 70, No. 2, 25 entitled, "Photolysis of Dibenzyl Ketone in Micellar Solution Correlation of Isotopic Enrichment Factors With

Photochemical Efficiency Parameters," discloses the enrichment of carbon 13 over carbon 12 by the photolysis of dibenzyl ketone using the fact that carbon 13 has a magnetic moment.

5        The use of magnetic nuclear moment to separate oxygen 17 from oxygen 16 and 18 is disclosed in an article by Nicholas J. Turro and Ming-Fea Chow, entitled, "Magnetic Isotope Effect on the Thermolysis of 9, 10-Diphenylanthracene Endoperoxide as a Means of Separation of 17 Oxygen  
10      from 16 Oxygen and 18 Oxygen," in the Journal of the American Chemical Society, Vol. 102; 3, January 30, 1980, pps. 1190 to 1192. An article by Kenneth L. Stevenson and James F. Verdieck in the Journal of the American Chemical Society, Vol. 90:11, May 22, 1968, pps. 2974 to 2975,  
15      entitled, "Partial Photoresolution Preliminary Studies on Some Oxalato Complexes of Chromium (III)," discloses that an aqueous solution of oxalato chromates can be enhanced in the cis or trans isomers when exposed to polarized light. The polarized light apparently partially dissociates only one of the isomers which then resolves into a  
20      racemic mixture.

Frederick A. Johnson, et al., in an article entitled, "Potassium Tetraoxalatozirconate (IV), Hafnate (IV) and Thorate Four in Inorganic Synthesis," Vol. 8, 25 pps. 40 to 44, 1966, discloses the preparation of tetraoxalatozirconate.

According to the present invention a method of altering the  $^{91}\text{Zr}$  isotopic content of zirconium comprises raising a zirconium chelate ligand from a ground state to an activated state in the presence of a scavenger which reacts with said ligand in said activated state but not in said ground state, permitting from 25 to 75% of said ligand to react with said scavenger, and separating said reacted ligand.

35        The invention includes a method of separating zirconium into a portion having a higher concentration of the  $^{91}\text{Zr}$  isotope and portion having a lower concentration

of the  $^{91}\text{Zr}$  isotope characterized by preparing a composition which comprises a zirconium chelate ligand; a solvent for said zirconium chelate ligand; and a scavenger which reacts with an excited state of said zirconium chelate ligand but not with its ground state; exciting said zirconium chelate ligand to said excited state; permitting from 25 to 75% of said zirconium chelate ligand to react with said scavenger; and separating said zirconium chelate ligand from the reaction product of said zirconium chelate ligand with said scavenger.

We have thus discovered that certain zirconium compounds can be used to effect the separation of the  $^{91}$  zirconium isotope from the remaining zirconium isotopes. Our process does not involve the use of a laser to excite particular absorption bands peculiar to certain isotopes. Unlike the laser isotope processes, which usually require a slow and very expensive gaseous reaction, the process of this invention can occur in an aqueous solution. As such, the process of this invention acquires considerably less capital equipment and is therefore much less expensive than the laser isotope processes.

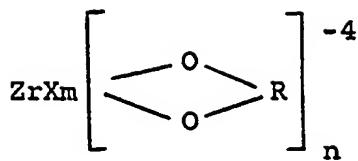
The present invention makes use of the fact that nucleons--protons and neutrons--have a spin and a magnetic moment. According to the rules of quantum mechanics, the spin of the nucleons can be in one of two directions, which means that the resulting magnetic moment can be in one of two directions. If there is an even number of nucleons, there is no overall magnetic moment on the nucleus because nucleons of opposite spin pair up, cancelling their magnetic moments. However, if the nucleus contains an odd number of nucleons, the unpaired nucleon will give the overall nucleus a small magnetic moment.

The electrons which surround the nucleus also have spins. When one atom is bonded to another atom, the spins of the electrons which form the bond are anti-parallel. But when the bond is broken, the spins relax so that they are no longer anti-parallel. Unless these spins

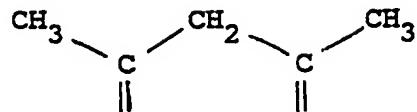
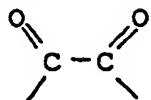
are anti-parallel, the two atoms which form the bond cannot recombine. It has been found that the rate at which the spins of electrons relax when a bond is broken depends on whether or not the atoms are in a magnetic field. It is believed that the spins relax faster when the atoms are in a magnetic field, but whether it is faster or slower, at least it is different. Since an isotope with an odd number of nucleons has its own magnetic field, this affects the relaxation rate of the electrons and therefore the rate at which a broken bond can recombine.

In this invention, a bond in a zirconium compound is broken and when broken, can undergo a reaction with another compound. Since zirconium 91 has an odd number of nucleons, it will have its own magnetic field which will relax the spins of the electrons in the broken bonds faster than the spins will relax in even-numbered isotopes such as zirconium 90. This means that the broken bonds in the zirconium 91 isotope will be slower to reform and therefore will be more likely to engage in a reaction with the scavenger compound than will the broken bonds of the even zirconium isotopes. As a result the original zirconium compound will become depleted in the zirconium 91 isotope and the reaction product of the original zirconium compound with the scavenger will become enriched in the zirconium 91 isotope. Since the reaction product is chemically different from the original compound, it can then be easily separated.

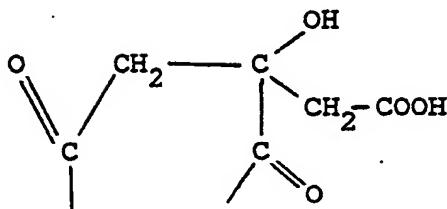
The class of zirconium compounds which we have found useful for separating the zirconium isotopes are known as zirconium chelate ligands. A zirconium chelate is an organic compound in which the atoms of the organic portion of the molecule are coordinated to a zirconium atom. The zirconium chelate is a ligand if each of the organic groups which is coordinated to the zirconium atom is coordinated by at least two bonds. The preferred zirconium chelate ligands may be described by the general formula:



where  $n$  is 3 or 4,  $m$  is  $2(4-n)$ ,  $X$  is halogen or cyanide, and  $R$  is

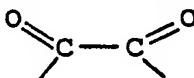


5 or



In the second  $R$  group given above there are three bonds to each oxygen atom, but this is acceptable because the electrons become delocalized over the whole ring. In the formula,  $n$  is preferably four and  $R$  is preferably

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The preferred compound is tetraoxylatozirconate (IV) (TOZ) because that compound is expected to work the best in the process of this invention.

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While the process of this invention could be conducted in a gaseous state, a major advantage of the invention is that it can be done in solution because solutions permit the use of much less expensive equipment and a much higher throughput than gases do. Many different solvents can be used to form the solutions such as  $\text{H}_2\text{O}$ , methanol, acetone, toluene, benzene, or tetra methyl formamide (TMF), but the solvent is preferably water as it is inexpensive, easy to work with, and does not absorb at the light wavelengths necessary to activate the zirconium chelate ligand. The solution preferably contains about 1 to 25% solids, though higher or lower concentrations may be used if desired.

A scavenger must be present which will react with the zirconium compound in its activated state but which will not react with the zirconium compound in its inactive or ground state. Suitable scavengers include 5 water, cyanide salts, ethylene diamine tetraacidic acid (EDTA), halide ions, or  $\text{SO}_4^{=}$ . The preferred scavenger is  $\text{Cl}^-$  because of its low cost and ease of handling and recycling. The amount of scavenger present is preferably from 90 to 110% (by weight) of the amount needed to 10 stoichiometrically react with all of the zirconium compound that is present.

Once the composition is prepared it is necessary to activate the zirconium compound, that is, to break a bond in the compound which can either recombine or react 15 with the scavenger. Activation may be accomplished with either heat or with light. The choice of optical or thermal excitation depends on the energy required to break the bond. The higher the required energy, the more favorable is optical excitation. For thermal excitation, the 20 fraction of molecules in an excited state  $E_i$  is proportional to  $e^{-E_i/kT}$  where  $k$  is Boltzmanns constant and  $T$  is the absolute temperature. For a temperature of 100°C,  $kT=741\text{cal/mole}(260\text{cm}^{-1})$ . Typically, electronic transitions in molecules require 10 to 1000 times the thermal energy 25 available at 100°C, so optical excitation is preferred as it gives a faster reaction. If heat is used, the temperature is preferably from 80 to 100°C as lower temperatures do not break bonds at a high enough rate and higher temperatures may break other bonds and lead to competing 30 reactions which are not isotope selective. If light is used, it preferably has a wavelength of from 220 to 350 nm. as the absorption bands of the relevant bonds lie within that wavelength range.

If the zirconium compound is activated for a 35 very long time, all of it will eventually react with the scavenger and there will be no separation of the zirconium isotopes. Therefore, the compound should be heated or

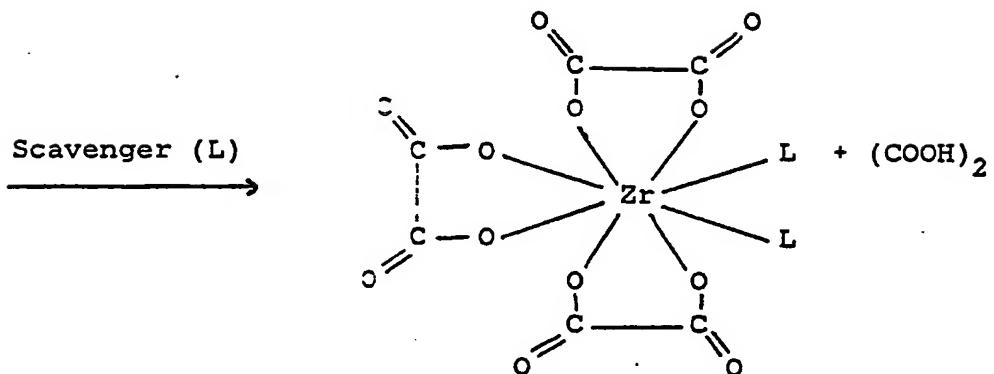
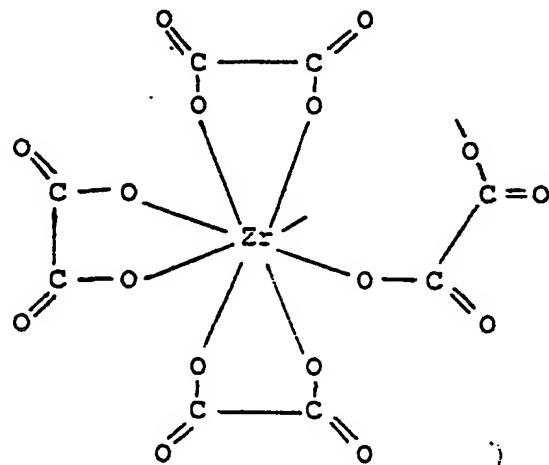
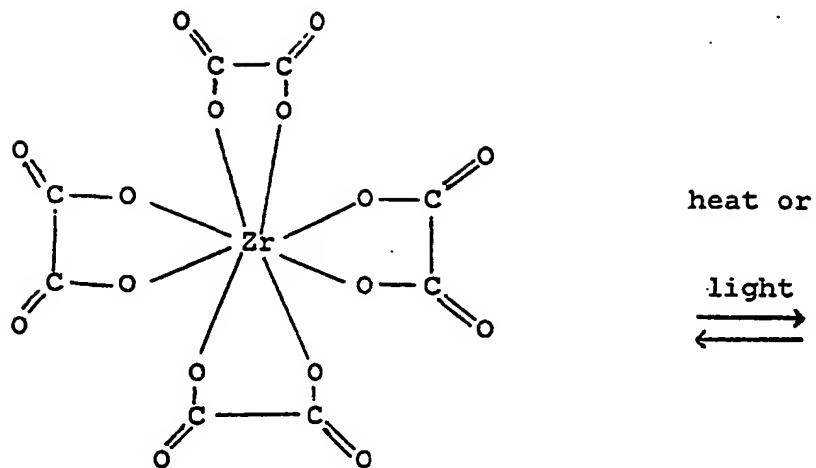
exposed to light only for a sufficiently long period of time to react from 25 to 75% of the amount of zirconium compound which is originally present. Preferably, only from 45 to 55% of the zirconium compound is reacted.

5 These ranges are selected to produce the optimum degree of separation between the zirconium 91 isotope and the other zirconium isotopes.

Optimization requires calculating the balance between the cost of preparing zirconium of a given isotopic 10 distribution and the value of reactor fuel saved by use of zirconium of that composition in the fuel cladding. Thus the optimum composition is based on economic rather than technical considerations.

Once the reaction has been terminated, the 15 reaction product of the scavenger and the zirconium compound can be separated from the unreacted zirconium compound by a variety of chemical techniques, such as ion exchange column, solvent extraction, precipitation, or high pressure liquid chromatography. The concentration of 20 the zirconium 91 isotope in the reaction product can be further enhanced, or its concentration in the unreacted zirconium further reduced, by repetition of the process of the invention. The unreacted zirconium can be used as is for fuel rod cladding or can be further enhanced in the 90 25 isotope using a laser isotope process.

While we do not wish to be bound by any theories, we believe that the following equations describe what is occurring in the process of this invention, using TOZ as an example.



The TOZ compound can be readily produced in solution by the addition of  $ZrOCl_2 \cdot 8H_2O$  to  $K_2C_2O_4 \cdot H_2O$  and  $H_2C_2O_4 \cdot 2H_2O$  as described in the Johnson Paper cited under prior art.

The invention will now be illustrated with 5 reference to the following Example:

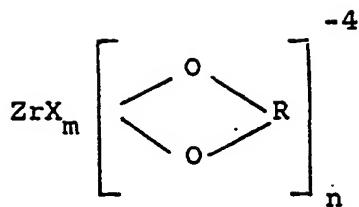
EXAMPLE

100g of  $K_4Zr(C_2O_4)_4 \cdot 5H_2O$  (TOZ, 0.14 moles) was dissolved in 1000 mil of water and 55g of  $Na_2H_2N_2(CH_2)_2(CH_2CO_2)_4$  (disodium EDTA, 0.14 moles) were 10 mixed in. The solution was irradiated with at  $\lambda = 254$  nm with a mercury arc lamp until 50% of the Zr complex had been converted to  $[Zr(C_2O_4)_3(EDTA)]^{-4}$ . The reaction 15 progress can be determined spectroscopically by monitoring the appearance of the product complex, the appearance of free oxalate, or the disappearance of free EDTA. When the reaction had progressed to the desired extent, the reaction was terminated by extinguishing the lamp.

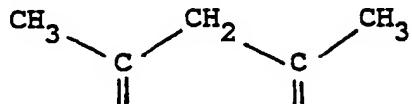
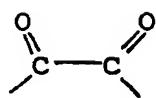
20 The starting complex and product complex were separated by passing the reaction mixture through an ion exchange column (eg. Dowex-1) and then eluting with 1M perchloric acid. It was determined that enrichment had occurred by mass spectroscopy.

## What we claim is:

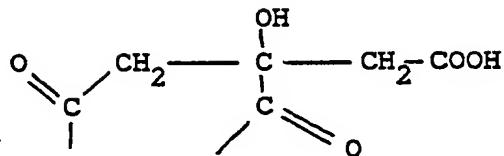
1. A method of altering the  $^{91}\text{Zr}$  isotopic content of zirconium characterized by raising a zirconium chelate ligand from a ground state to an activated state in the presence of a scavenger which reacts with said ligand in said activated state but not in said ground state, permitting from 25 to 75% of said ligand to react with said scavenger, and separating said reacted ligand.  
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2. A method according to claim 1, characterized in that the reaction occurs in solution.  
10
3. A method of separating zirconium into a portion having a higher concentration of the  $^{91}\text{Zr}$  isotope and portion having a lower concentration of the  $^{91}\text{Zr}$  isotope characterized by preparing a composition which comprises a zirconium chelate ligand; a solvent for said  
15 zirconium chelate ligand; and a scavenger which reacts with an excited state of said zirconium chelate ligand but not with its ground state; exciting said zirconium chelate ligand to said excited state; permitting from 25 to 75% of said zirconium chelate ligand to react with said scavenger;  
20 and separating said zirconium chelate ligand from the reaction product of said zirconium chelate ligand with said scavenger.  
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4. A method according to claim 3, characterized in that the zirconium chelate ligand has the general formula



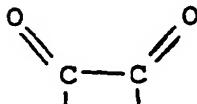
where  $n$  is 3 or 4,  $m$  is  $2(4-n)$ ,  $X$  is halogen or cyanide, and  $R$  is



5 or



5. A method according to claim 4, characterized in that  $n$  is 4 and  $R$  is:



10 6. A method according to claim 3, 4 or 5, characterized in that the zirconium chelate ligand is excited with light having a wavelength of from 220 to 350 nm.

15 7. A method according to claim 3, 4 or 5, characterized in that the zirconium chelate ligand is activated by heating to from 80 to 100°C.

8. A method according to any of claims 3 to 7, characterized in that the solvent is water.

20 9. A method according to any of claims 3 to 8, characterized in that the composition is from 1 to 25% solids.

10. A method according to any of claims 3 to 9, characterized in that the concentration of the scavenger is from 90 to 110% of stoichiometric.

11. A method according to any of claims 3 to 10, characterized in that from 45 to 55% of the zirconium chelate ligand is permitted to react with said scavenger.

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## EUROPEAN SEARCH REPORT

Application number

EP 82 30 2854.3

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>2</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US - A - 2 892 681 (H.W. CRANDALL et al.) -----		B 01 D 59/34
			TECHNICAL FIELDS SEARCHED (Int.Cl. <sup>3</sup> )
			B 01 D 59/00 C 01 G 25/00 C 22 B 34/00 G 21 C 3/00 G 21 C 21/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons  &: member of the same patent family, corresponding document
<input checked="" type="checkbox"/>	The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner	
Berlin	30-08-1982	BERTRAM	